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The temperature coefficient of the potential of zero charge of Ag single crystal face electrodes in aqueous electrolyte solution*

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The temperature coefficient of the potential of zero charge of Ag single crystal electrodes, $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$, was measured by recording capacitance curves at different temperatures. Two experimental approaches were adopted: the “continuity” and the “discontinuity” method, consisting in recording curves at different temperatures without and with extraction of the electrode from the solution, respectively. Appreciable differences have been observed. The origin of the differences and their significance are discussed in terms of keeping the appropriate conditions for the electrode/solution interface during the experiments.

Key words: *silver, single crystal electrode, potential of zero charge, effect of temperature, work function, electrical double layer*

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1. Introduction

An electrode is constituted by an electronic conductor (usually a metal) in contact with an ionic conductor (electrolyte). Conversion of electrical energy into chemical energy (electrolyzers) and *vice versa* (power sources) occurs *via* charge-transfer reactions across the electrode interface.

The rate and mechanism of the reactions occurring at electrodes are essentially influenced by the structure of the metal/solution phase boundary [1]. The latter depends on a number of variables: nature and structure of the metal surface, nature of the solvent and the electrolyte, temperature and interfacial electric field (electrode

*Dedicated to Professor J.P.Badiali on the occasion of his 60^{th} birthday.

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potential) [2]. The interfacial region is customarily called "electrical double layer" in view of the local separation and regular distribution of free charges on the surface regions of the two phases in contact [3].

Knowledge of the structure of the electrode interface is crucial to understand the mechanism and the kinetics of electrode reactions. Experimental studies in that direction started at the beginning of last century with the measurements of the interfacial tension of Hg and the application of the Gibbs adsorption equation by Gouy [4]. Later, with the advent of electronics, interfacial tension measurements were supplemented by capacitance measurements, especially thanks to the studies of D.C.Grahame [5], in which the interface responds as an electrical condenser.

Hg ceased to be the only metal used for interfacial studies in the 1960's as the Soviet School headed by Academician A.N.Frumkin introduced the use of other liquid metals (e.g., Ga and Ga alloys with In and Tl) and of non-catalytic solid sp-metals (Cd, Sn, Pb, Bi, Zn, In, Tl) [2,6]. Later in those years, the French [7] and Bulgarian [8] schools started the study of single crystal face electrodes, essentially Au and Ag.

Experimental studies were paralleled by modelling of the interfacial region throughout the years. Thus, the first model of electrochemical interface proposed by Helmholtz in the 1870's (two rigid layers of charges) was followed by the model of Gouy-Chapman (1910) [9] (the distribution of charges on the solution side is diffuse but point charges are considered), as corrected by Stern (1924) [10] (ions are not point charges but they have finite size), and improved by Grahame (1947) (positive and negative ions are differently solvated so that their distances of maximum approach to the electrode surface differ) [11].

Successive models have introduced a number of complexities to account for the asymmetry of the capacitance curves with respect to the charge sign, as well as for the effect of the nature of the metal [2]. However, in these models all the variation of experimental parameters is attributed to the properties of the solution side of the interface, while the solid surface is considered to be a perfectly plane, homogeneous, equipotential, structureless boundary. The approach was modified by the work of Professor Badiali [12–14] who in the early 1980's introduced the atomic and electronic structure of the metal surface into his model through the use of pseudo-potentials. His work opened a new direction in the modelling of electrochemical interfaces. Later, other authors used the jellium model to theoretically describe the metal surface [15].

The predictions of models have to be checked against experimental results. The structure of the electrode interface governs a number of experimental parameters, in particular the electrode potential. As described below, the potential of zero charge, $E_{\sigma=0}$ i.e., the potential in the absence of an externally applied electric field, is closely related to the electronic structure of the metal. Thus, $E_{\sigma=0}$ links electrochemistry with condensed matter physics more directly than any other electrochemical parameter [16].

$E_{\sigma=0}$ depends on the structure of the solvent on the solution side of the interface and such an effect is exalted by the effect of a change in the temperature [17].

For the above reasons, the mode of interaction between water molecules and a well defined metal surface is studied in this work by measuring the potential of zero charge of Ag single crystal faces in aqueous solutions of surface inactive electrolytes as a function of temperature. More in particular, it is shown that the procedure adopted to measure $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$ can crucially influence the experimental results thus potentially misleading the interpretation of the data.

2. Experimental

Two types of Ag single crystals were used: (a) rods of 3 mm diameters grown, oriented and cut at LEI, CNRS (Bellevue) in collaboration with Dr. A.Hamelin during a previous stay of L.M.D., and (b) cylinders of 10 mm diameter and 30 mm length as received from the manufacturers (Goodfellows). Both types of electrode surfaces were pretreated using a procedure of chemical etching based on an acidic solution of CrO_3 [18]. The effectiveness of this route has been demonstrated in previous papers [19–22].

KPF_6 was used as an electrolyte because of its demonstrated surface inactivity around the potential of zero charge over the usually explored concentration range (0.005 to 0.1 mol dm^{-3}). KPF_6 was purified as described elsewhere [23]. Aqueous solutions were prepared volumetrically by dissolving KPF_6 in ultrapure Millipore water (Milli RO + MilliQ system).

The contact between the electrode surface and the solution was made in the electrochemical cell by the hanging meniscus method [24]. The solution was deaerated by bubbling ultrapure N_2 for at least 30 min before starting experiments. During measurements the atmosphere of the cell was kept under N_2.

The structure and the cleanliness of electrode surfaces were checked by cyclic voltammetry and capacitance-potential curves using literature data and our own previous data as reference data. A glassy carbon stick was used as an auxiliary electrode. The reference electrode was a commercial (AMEL) saturated calomel electrode (SCE), separated from the cell main compartment by a Luggin capillary and a glass frit to avoid any possibility of Cl^- pollution of the solution.

The temperature of a water bath was controlled to ± 0.1°C by a thermostat, the cell being immersed in the bath. Measurements were carried out both in isothermal and non-isothermal cell arrangements.

Several measurements were carried out with the same electrode, and several electrodes were used with the same crystallographic orientation. The reproducibility of the data will be shown hereinafter. Also, experiments with electrodes having the same crystallographic orientation but differently prepared were purposely carried out.

Electrochemical experiments were carried out using a Model 273A EG&G potentiostat/galvanostat coupled with a Model 5210 EG&G lock-in amplifier for capacitance measurements. Details about the experimental procedures have been given elsewhere [25].

As already mentioned in a previous paper of us [20], the most crucial point has

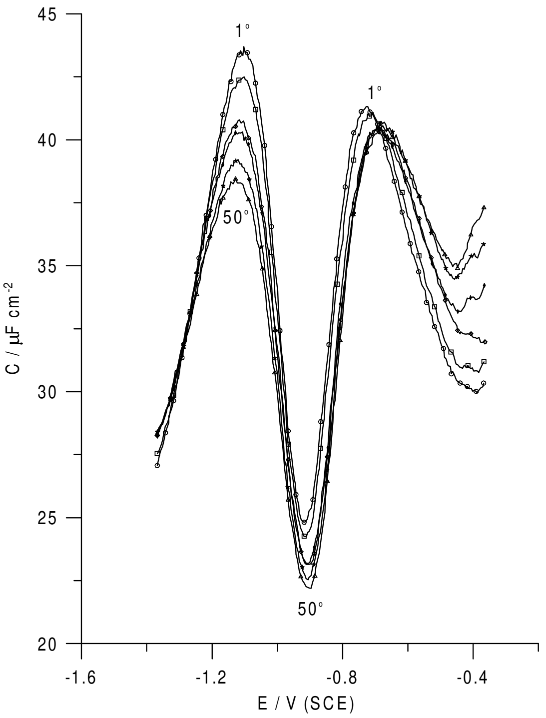

Figure 1. Capacitance-potential curves of a Ag (311) electrode in 0.02 mol dm^{-3} KPF_6 aqueous solution at six different temperatures between 1 and 50°C. "Continuity" method.

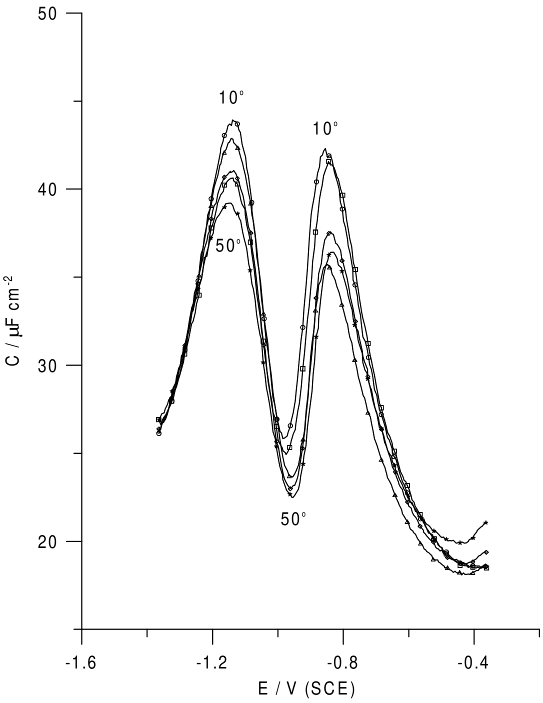

Figure 2. Capacitance-potential curves of a Ag (110) electrode in 0.02 mol dm^{-3} KPF_6 aqueous solution at five different temperatures between 10 and 50°C. "Continuity" method.

been found to be the sequence of temperature variation. Two approaches were adopted: (a) Pre-treated electrodes were immersed in the solution at a given temperature, the curve recorded and a new temperature fixed without removing the electrode from the solution [26]. In this way an entire family of curves at different temperatures was recorded ("continuity" method); (b) Pre-treated electrodes were immersed in the solution at a given temperature, the curve recorded and the electrode removed before fixing another temperature [20]. As the new temperature was established, the newly pre-treated electrode was immersed again in the solution, and the new curve recorded. The time elapsing between two measurements at different temperatures and the pre-treatment between two measurements ensured that the curves at two temperatures can be regarded as two totally unrelated experiments ("discontinuity" method).

3. Results

Capacitance-potential curves of metal electrodes in dilute electrolyte solution are typically characterized by a deep minimum [19], whose depth increases with electrolyte dilution, which in the absence of ionic specific adsorption identifies the

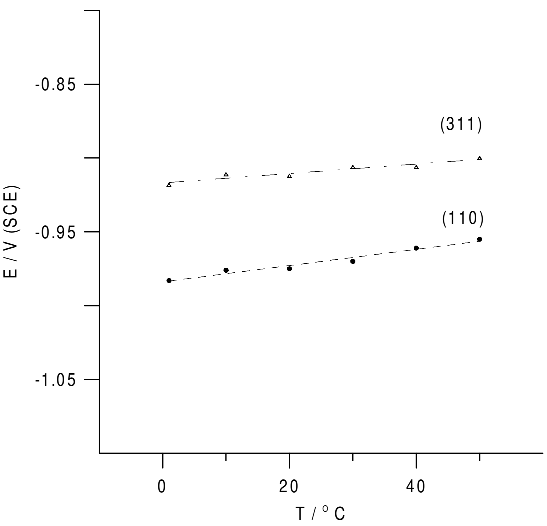

Figure 3. Plot of the potential of the capacitance minimum in figures 1 and 2 as a function of temperature. "Continuity" method.

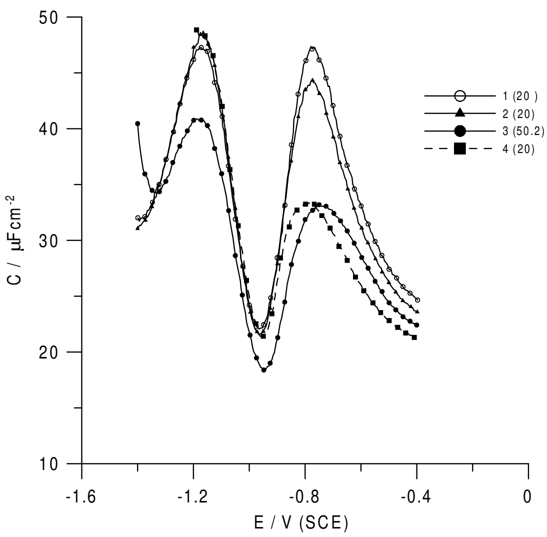

Figure 4. Capacitance-potential curves of a Ag (110) electrode in 0.01 mol dm^{-3} KPF_6 aqueous solution recorded at 20°C with the "continuity" method at different stages of a continuous temperature scan. (1) Initial curve; (2) After going to 0°C and back to 20°C; (3) At 50°C after rising the temperature from curve (2); (4) After lowering the temperature from curve (3).

potential of zero charge [16]. Necessary and sufficient condition to rule out specific adsorption around the potential of zero charge is the independence of $E_{\min}$ of the electrolyte concentration. This has been proved in the case of KPF_6 for various Ag single crystal faces in previous papers [19,27]. Therefore, $E_{\min}$ in 0.01–0.02 mol dm^{-3} solutions of KPF_6 has been identified with the potential of zero charge, $E_{\sigma=0}$.

Figure 1 shows a typical family of capacitance curves for a (311) Ag electrode at temperatures between 1°C and 50°C. This set of experiments was carried out using the method of "continuity". The curves appear well ordered with the typical negative temperature coefficient of capacitance (C decreases as temperature increases) over most of the potential range with the exception of the positive extreme, as observed also with Au single crystal electrodes [28]. However, such a detail may not appear, as shown in figure 2 where a family of capacitance curves for the (110) face, also obtained by the method of "continuity", exhibits a negative temperature coefficient all over the potential range except the negative extreme where the curves merge.

In the both mentioned cases, $E_{\min}$ is clearly seen to shift toward more positive values as the temperature is increased, i.e., $\mathrm{d}E_{\sigma=0}/\mathrm{d}T > 0$. This outcome is more evident in figure 3 where $E_{\sigma=0}$ for both (311) and (110) faces is plotted against the temperature. The scatter of points around a common straight line is higher for the (311) face but there is no doubt that $\mathrm{d}E_{\sigma=0}/\mathrm{d}T > 0$ in both cases, in particular it is higher for the (110) face.

Some puzzling effects of the "continuity" method on the capacitance curves are evident in figure 4. The data refer to the

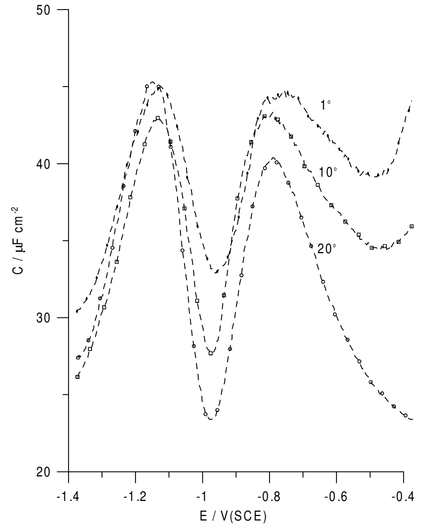

Figure 5. Capacitance-potential curves of a Ag (110) electrode in 0.02 mol dm^{-3} KPF_6 aqueous solution at three different temperatures. "Discontinuity" method.

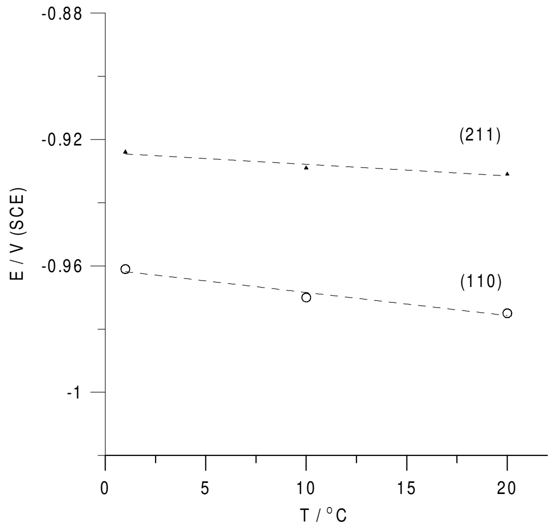

Figure 6. Plot of the potential of the capacitance minimum for a (110) and a (211) Ag face as a function of temperature. "Discontinuity" method.

(110) face of Ag in 0.01 mol dm^{-3} KPF_6 solution. When working in a continuous way it is as a rule preferred to move from lower to higher temperatures since diffusion of (organic) impurities to the electrode surface is enhanced by temperature. Therefore, it is convenient to stay in the higher temperature range as shortly as possible. Thus, experiments are usually started at room temperature (20°C in this work) moving first to lower and then to higher T.

If the first curve at 20°C is taken as a reference, figure 4 shows that after going to 0°C and back to 20°C, curve 2 is already somewhat different from curve 1 although both at the same temperature with the same meniscus configuration. In particular, the height of the right-hand peak is lower, while the position of the minimum (identified with $E_{\sigma=0}$) is, however little, shifted to a more positive value.

Curve 3 in figure 4 shows the capacitance curve at 50°C. The maximums are lower with the capacitance minimum at more positive potentials, but an increase presumably related to incipient hydrogen evolution appears on the extreme negative side, which points to a different state of the surface from the initial one. This view is corroborated by curve 4, which is again at 20°C after cooling down the solution with the electrode in place. It is intriguing that the maximum on the positive side of the minimum does not go back to the initial value but remains suspiciously close to its value at 50°C. Moreover (and especially) the potential of the capacitance minimum is clearly pushed to a more positive value.

The results in figure 4 definitely show that the "continuity" method is affected by hysteresis effects which can alter the actual dependence of $E_{\sigma=0}$ on temperature. Such an effect has been above attributed to adsorption of (organic) impurities which are known to (as a rule) shift the potential of zero charge of metal electrodes to more positive values. However, other factors have also to be considered, such as slight surface reconstruction under the action of temperature, and modifications in the geometry of the solution meniscus with a change in the parameters of the interfacial region.

Figure 5 shows a family of capacitance-potential curves for Ag (110) as obtained by the "discontinuity" method. Looked at singly, the curves exhibit the same shape as those of figures 1 and 2. However, as a family, they are less homogeneous and more scattered. In particular, the potential of zero charge shifts toward more negative values as the temperature is increased. This is shown more in detail in figure 6 where $E_{\sigma=0}$ is plotted as a function of temperature. A negative value of $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$ for the (110) face has been obtained also with a disc electrode thus confirming previous findings [20], and has been observed also with the (211) face, always with the method of "discontinuity". A positive value of $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$ for the (110) face with the method of "continuity" has also been obtained in independent experiments by another operator [26].

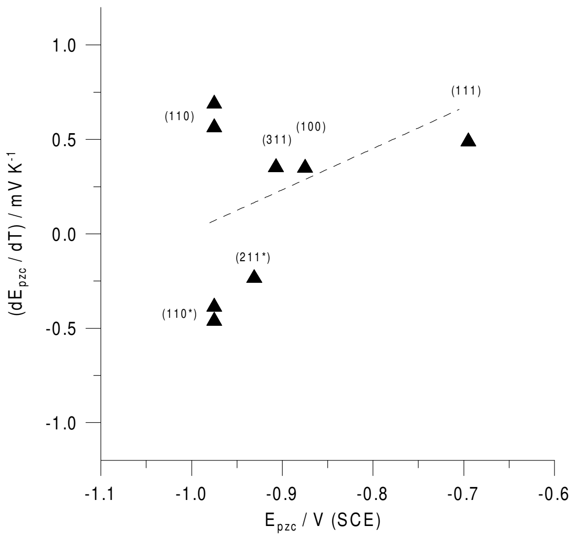

Figure 7. Plot of the temperature coefficient of the potential of zero charge of different Ag crystal faces as a function of the potential of zero charge at 20°C. Asterisk: "Discontinuity" method.

The values of $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$ obtained in this work, together with the previous results collected by the same authors, are plotted in figure 7 against the value of the potential of zero charge. Although scattered (and it cannot be different in view of the effect of the experimental methodology), a trend for $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$ to increase with increasing $E_{\sigma=0}$ can be recognized. This trend does not show any systematic decrease of $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$ for stepped surfaces of Ag as claimed in the case of Au single crystal electrodes [29].

Capacitance data were further worked out to derive the entropy of formation of the interface, S^*, according to a procedure described by Silva and coworkers [30]. The results are shown in figures 8 and 9 for the "continuity" and the "discontinuity" method, respectively. The curves in figure 8 exhibit the same shape as those of Au. More specifically, S^* is positive only in a range of negative charges with a maximum around -5 μC cm^{-2}, a value comparable to that for Au. Further, the values of S^*, in the charge range where they are negative, decrease in the order (111) > (100) > (110), also in qualitative agreement with the behaviour of Au single crystal faces [28].

The curve in figure 9 is also parabolic, although the shape is less regular, as a consequence of the higher scatter of the experimental data as noted above. It is

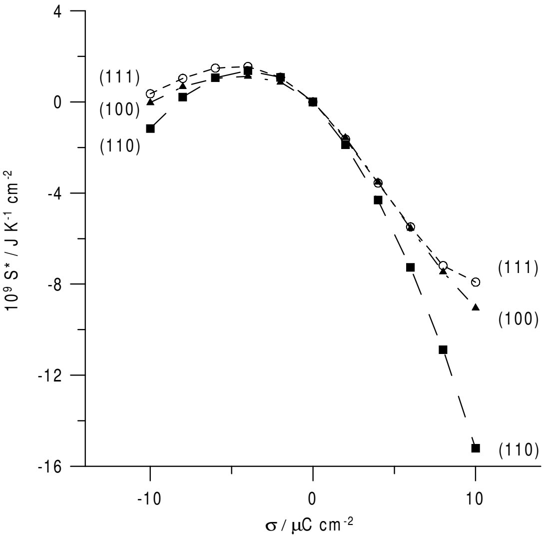

Figure 8. Dependence on charge of the entropy of formation of the electrical double layer for different Ag single crystal faces. "Continuity" method.

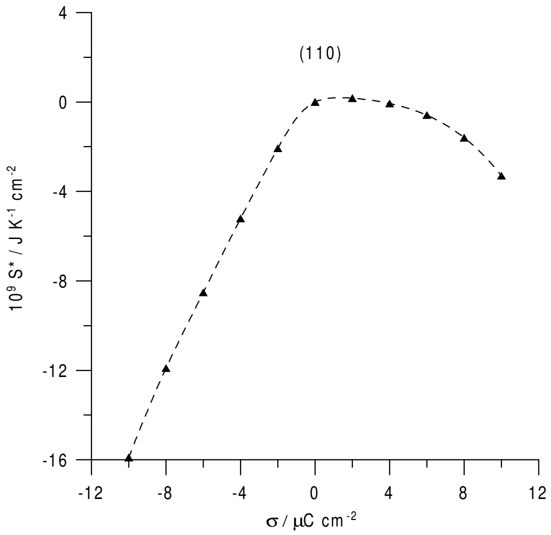

Figure 9. Dependence on charge of the entropy of formation of the electrical double layer for a Ag (110) single crystal face electrode. "Discontinuity" method.

therefore more difficult to obtain information about the quantitative behaviour of S^*. On the other hand, further experiments are necessary to compare the results of the "discontinuity" method for different crystal faces.

4. Discussion

The nature of the component of an electrode interface has been discussed in several previous papers. It has been demonstrated that the measured electrode potential is a relative value (vs. a reference electrode) of the electron work function of the metal phase as modified by the solution phase [31]. Thus, if an electron is taken from the Fermi level of the metal electrode to infinity when the metal phase is uncharged, the work is given by:

$$\mathrm{e}E_{\sigma=0} = \Phi + \delta\Phi + \mathrm{e}\chi^S + \mathrm{e}\delta\chi^S + K_{\mathrm{ref}}\,, \tag{1}$$

where Φ is the electron work function of the metal in a vacuum, $\delta\Phi$ is the modification of Φ as the metal comes in contact with the solution, χ^S is the surface potential of the isolated solution, $\delta\chi^S$ is its modification upon contact with the metal, and K_{ref} is the contribution due to the reference electrode (a constant at constant temperature). Thus, if the temperature is varied [17]:

$$\mathrm{ed}E_{\sigma=0}/\mathrm{d}T = \mathrm{d}\Phi'/\mathrm{d}T + \mathrm{ed}g^S_{\mathrm{dip}}/\mathrm{d}T + \mathrm{const}, \tag{2}$$

where Φ' is the electron work function as modified by the presence of the solution, and $g^S_{\mathrm{dip}} = \chi^S + \delta\chi^S$ is the potential associated with the dipolar layer of solvent molecules at the interface with the metal.

There is no way to determine separately $\delta\Phi$ and g^S_{dip}, although their sum determines the variation of Φ and can be measured experimentally in principle [16]. Thus, there is no way to separate the electronic contribution from the solvent contribution in equation (1) experimentally.

For long $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$ was interpreted only in terms of solvent contribution neglecting any contribution from the metal surface. Trasatti [17] was the first to warn against this approach. Since solvent molecules are usually preferentially oriented with the oxygen atom toward the metal surface, a simple model of a reorienting dipole layer would predict a positive value for $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$ since the disorganizing effect of temperature would result in a less negative value of g^S_{dip}. For this reason, negative values of $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$ have been considered puzzling. Trasatti has shown that in equation (2) $\mathrm{d}\Phi'/\mathrm{d}T$ is usually negative while $\mathrm{d}g^S_{\mathrm{dip}}/\mathrm{d}T$ is positive. Thus, a negative value of $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$ is in principle possible if the electronic term prevails over the dipolar term, i.e., $\mathrm{d}g^S_{\mathrm{dip}}/\mathrm{d}T$ is small.

The simple model of reorienting solvent dipoles with neglection of electronic contributions (in other words of electronic entropy terms), besides predicting positive values of $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$ for negative values of g^S_{dip}, also predicts that the higher g^S_{dip} the higher the positive values of $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$. This has led Silva et al. [32] in the case of Au single crystals to conclude that water molecules are more oriented (i.e., the metal-water interaction is stronger) on the (111) face than on the (110) face as an explanation of the more positive value of $\mathrm{d}E_{\sigma=0}/\mathrm{dT}$ for the (111) face. This interpretation has been questioned by the present authors [31] on the ground that the model of a dipolar layer is valid only for non-interacting particles, especially with the metal surface. It seems evident that if metal-water interactions are strong, the orientation of water dipoles will be stronger while for the same reasons the disorganizing effect of temperature will be weaker. Thus, $\mathrm{d}g^S_{\mathrm{dip}}/\mathrm{d}T$ will be more positive the weaker the metal-water interaction through the oxygen atom of water molecules is.

The same remark applies also in the case of the interpretation of the charge dependence of S^*. According to Silva et al. [29], a stronger metal-water interaction should lead to a more positive value of S^* as the bond is weakened by an electric field. According to the present authors, the stronger the metal-water surface chemical bond, the weaker the effect of an electric field, as discussed above in the case of the sign of $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$.

In previous work [31] it has been shown that equation (1) can also be written as:

$$\mathrm{e}E_{\sigma=0} = \Phi + \Delta X + \mathrm{const}, \tag{3}$$

where ΔX, called the interfacial term, measures the variations occurring at the interface as the metal comes in contact with the solution (at zero charge). In other words, the higher ΔX, the stronger the modifications occurring at the interface, i.e., the stronger the metal-water interactions. Since ΔX can be estimated [16] from a plot of Φ (as measured in surface physics) against $E_{\sigma=0}$ as measured in electrochemistry, the experimental picture is consistent with $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$ becoming more positive as ΔX decreases, i.e., as metal-water interactions become weaker, which supports the qualitative arguments given above.

This work has demonstrated that the experimental procedure used in measuring $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$ is apparently at the base of pieces of experimental evidence leading to misleading arguments to interpret the data. The reason why the "discontinuity" method should be more reliable than the "continuity" method is very simple: if a single capacitance curve is recorded at a given temperature, there is not a single reason to reject the experiment. Thus, that curve is accepted in the literature. If the same experiment is repeated at different temperatures on different days, there is not a single reason to question a temperature simply because it is above or below the room temperature. Thus, with the "discontinuity" method if a curve at 25°C is customarily accepted, curves should be accepted at any other temperature. Therefore, the temperature coefficient of $E_{\sigma=0}$ obtained by the "discontinuity" method is as reliable as the single curves. However, what is evident is that the method suffers from poorer reproducibility because all the experimental variables are renewed from experiment to experiment.

These conditions are less stringent in the case of the "continuity" method and precisely for the same reasons the family of curves is more homogeneous. However, experiments have shown that from a temperature to another the electrode is probably affected (or influenced) by its previous history. Some of these aspects have been discussed in a previous overview of the problem [31].

5. Conclusions

1. The magnitude and sign of the temperature coefficient of the potential of zero charge of Ag single crystal face electrodes depend on the experimental procedure of measurement of capacitance curves at different temperatures.

2. Measurements carried out by means of the "discontinuity" method, i.e., by recording capacitance curves at different temperatures quite independently from one another, are considered globally reliable since each curve, singly taken, possesses the same reliability. Measurements carried out by means of the "continuity" method are potentially affected by the previous history of the electrode surface (i.e., by the immediately preceding temperature). It is to be recalled that measurements in both cases were taken using the hanging meniscus to create the electrode/solution interface.

3. Evidence has been shown for a positive increase in $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$ as $E_{\sigma=0}$ becomes more positive. Since electronic (metal) and dipolar (solution) contributions of opposite sign are operative in determining $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$, the experimental evidence is taken to indicate a higher value of the dipolar contribution (solvent) the weaker the metal-water interactions are. Thus, contrary to the views of other authors [29], [32], it is here demonstrated that metal-water interactions increase in the sequence (111) < (100) < (110), i.e., in the opposite order of the values of $\mathrm{d}E_{\sigma=0}/\mathrm{d}T$.

6. Acknowledgements

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Температурний коефіцієнт потенціалу нульового заряду срібних монокристалічних електродів у водному розчині електролітів

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На основі даних для ємності при різних температурах отримано температурний коефіцієнт потенціалу нульового заряду срібних монокристалічних електродів. Застосовано два типи експериментів: метод “неперервності” і “розривності”, що полягає в записі кривих ємності при різних температурах без і з виділенням вкладу електрода в розчині відповідно. Виявлена суттєва різниця в результатах, походження і важливість якої досліджується при відповідних умовах експериментів для поверхні розділу електрод-розчин.

Ключові слова: *срібло, монокристалічний електрод, потенціал нульового заряду, вплив температури, робота виходу, подвійний електричний шар*

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